Rapid Synthesis in a Microcombustion Environment and Transfer Process Development for Few Layer Graphene

A Senior Honors Thesis

Presented in Partial Fulfillment of the Requirements for Graduation with Distinction in the Department of Mechanical and Aerospace Engineering in the Undergraduate Colleges at The Ohio State University

By

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ABSTRACT

Graphene is a nanomaterial that consists of a carbon monolayer (one atom thick) arranged in the graphitic structure. Since the 2004 discovery of graphene as a material useful for applications using nanotechnology, there has been significant interest in the synthesis and applications of graphene. Possible applications focus on areas that utilize the excellent properties of graphene for high electrical conductivity, stronger composite materials, and increased rate of fluid flow through graphene. However, current methods for synthesis are either not easily scalable for industrial production or require complex, slow, and expensive methods. Recent work has shown that microcombustion presents a novel, rapid, and efficient method for targeted graphene synthesis. The objective of this undergraduate honors project is to deposit few layer graphene (FLG) on Cu (copper) wires and then transfer these to a silicon substrate for application in a biosensor towards prostate cancer cell detection. Several experimental methods for transferring FLG layers from Cu wires were compared and evaluated. After each test, Si samples were analyzed using Raman spectroscopy to check for chemical integrity and scanning electron microscopy (SEM) to identify size and structure. Each method had pros and cons. For instance, chemical etching of Cu wires adhered to Si substrates with adhesive led to Si fouled by etched particles and adhesive residue. Attempts to dissolve the adhesive by solvent treatment led to encapsulation of FLG layers with the adhesive. Sonicating Cu wires to release FLG followed by filter collection has shown ability to collect small flakes with size yet to be determined. Unfortunately, filter capture requires a high degree of precision and an elaborate set-up to achieve successful transfer. Due to these obstacles, successful transfer and implementation of FLG into an application was not achieved. Additional work is required to further the work and results seen in the project and create a robust transfer process for the FLG flakes.

DEDICATION

To my Grandfather Ralph and in memory of my Great-Uncle Joe.

Two men from an earlier generation of engineers, both of whom have provided me with wonderful role models and have inspired me to pursue my education to the fullest.

ACKNOWLEDGEMENTS

I would like to thank Dr. Shaurya Prakash and Dr. Robert Siston for providing continuing support, encouragement, and guidance during my first foray into the exciting world of research. Additionally, I would like to thank Ben Kellie for many insightful and candid discussions of a wide range of topics, pertaining to the project and otherwise. I would also like to thank Dr. Gordon Renkes of the Analytical Spectroscopy Laboratory, Ms. Karen Bellman, and Ms. Marie Pinti for all of their assistance with sample analysis and imaging. Finally, I would like to thank all of the researchers at the Microsystems and Nanosystems (MSNS) Laboratory as well as my classmates in ME 4999H for their support and endless feedback throughout the duration of the project. Financial support or in-kind services were provided by the following companies and institutions: The Ohio State University, The Ohio State University College of Engineering, and the MSNS Laboratory.

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1. INTRODUCTION

1.1 Purpose

Previous work in the Prakash group has shown microcombustion reactors to be an effective and novel means of synthesizing graphene [1]. When compared with current methods of graphene synthesis, this new method shows promise for rapid and a comparatively simple method for synthesis of graphene. In order to effectively develop applications, transfer of graphene to a suitable substrate from the substrate used for synthesis (i.e. the synthesis and application substrates are usually different) for the desired application must be achieved. In order to ensure pristine graphene and best results in application, the transfer process required must not damage or contaminate the graphene. The purpose of this project is to develop a robust transfer process for few layer graphene (FLG) to a silicon wafer as it is a substrate used in several applications. Once an effective transfer process has been devised, the FLG is to be implemented into a biosensor application for the detection of prostate cancer cells.

1.2 Introduction to Graphene

Graphene consists of a monolayer (one atom thick) of carbon in the graphitic structure and forms in large ~2D sheets with grain growth dependent on synthesis substrate grain boundaries. [2]. The atomic structure can be seen in Figure 1 and a scanning electron microscope image (SEM) can be seen in Figure 2. Graphene was discovered in 2004 and has garnered a large amount of interest due to the favorable and exceptional properties that it exhibits [3, 4].

Recent work with graphene has focused in the areas of high electrical conductance, high young's modulus, and increased rate of fluid flow across graphene surfaces. All of these properties indicate areas of application for graphene, this project intends to utilize graphene's

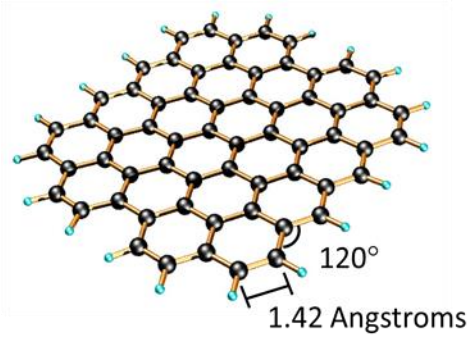


Figure 1: Atomic structure of graphene [5], the black spheres represent C molecules, brown bands indicate C-C covalent bonds, and blue dots simply indicate the locations where the repeating structure was truncated.

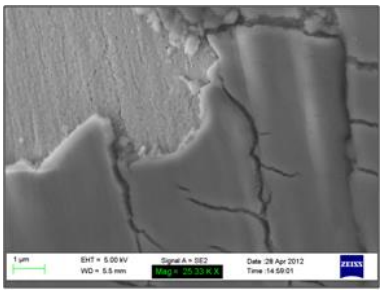


Figure 2: Graphene deposited on a Cu substrate. FLG was synthesized in a microcombustor at a 756 sccm flow rate (531 sccm CH_4 - 225 sccm O_2) with a 20 s deposition time.

high electrical conductance for the creation of a cancer sensor that is more sensitive than traditional sensors. Graphene's high electrical conductance is a direct consequence of the high level of electron mobility exhibited throughout the carbon sheets.

Graphene has been estimated to have an electron mobility of 15,000 $cm^2\ V^{-1}\ s^{-1}$[3, 4], while other semiconductors such as silicon (Si) exhibit electron mobility of 1,400 $cm^2V^{-1}s^{-1}$ or an increase greater than an order of magnitude. Additionally, Graphene has exhibited a tensile Young's modulus in the planar direction of ~ 1 TPa, which is five times greater than that of steel (200 GPa) [6]. This has led to work focusing on the use of graphene as a promising material for composite materials, such as graphene reinforced polymers [7]. Finally, theoretical work has

indicated that graphene membranes may have the ability to exhibit higher fluid flow rates through the membrane than classical materials [8]. With cross membrane pressure held constant, flux through a membrane scales inversely with the membrane thickness; this relationship identifies extremely thin and strong materials such as graphene as ideal candidates for membrane materials [8]. Additionally, nanomaterials such as graphene, due to their periodic molecular structure, present well defined channels for convective fluid flow which is two orders of magnitude faster than traditional diffusion processes [8]. This has led to interest in implementing graphene membranes within water desalination units with hopes for increased process efficiencies and an increase in gallons per process hour.

The main obstacle to implementing graphene to the wide variety of applications mentioned above is long and complicated synthesis methods. Graphene was discovered through a method known as mechanical cleavage [4]. Thin layers of graphene were sheared using scotch tape from bulk graphite. These layers were sheared again and again in a similar manner to reduce sample thickness until a single layer was achieved [4]. Unfortunately, due to surface roughness of bulk graphite and the ensuing small flake sizes (~10 μm), this process is not scalable for industrial production of graphene.

The primary method of synthesis that has gained popularity in recent years is chemical vapor deposition (CVD) due to the ability of CVD to produce large sheets (~5 cm x 5 cm) of highly ordered graphene [9-12]. During this process, hot reactant gases are blown over a heated substrate and gaseous carbon particles are deposited upon the substrate. These carbon particles agglomerate and become a solid upon the substrate. In the case of graphene, the reaction gases are typically hydrocarbons such as methane and may or may not be mixed with other neutral gases. While CVD is an effective method of synthesis, ease of synthesis is limited by long

process times, low process efficiencies [13], and complicated experimental setups such as vacuum sealed chambers that are required by CVD.

1.3 Graphene Synthesis in a Microcombustor

The Prakash group has demonstrated through recent work that synthesis of graphene in a microcombustor is possible and is a viable means of rapid synthesis for graphene [14]. Microcombustion is characterized by combustion in which the surface area of the flame is greater than the volume of the flame. After ignition, this flame structure is initially dominated by a hydrodynamic instability and only reaches stability once the combustor walls reach a critical temperature (nearing combustion temperature) which sustains the flame [15-17]. Once the flame reaches a stable state, previous work has shown steep temperature gradients and convective eddies which enhance mixing cause the mixing region for the laminar flame to be outside of the mean free path of the reactant flows [18-20]. This phenomenon allows combustion efficiency to be enhanced and controlled. Combining methane (CH_4) and oxygen (O_2) fuel and increased combustion efficiency, the flame produces an exhaust flow that is rich in gaseous C radicals (C atoms that have not combine with other exhaust atoms to form exhaust products such as CO_2, CO, etc.) which is similar to the synthesis environment seen in CVD systems. An exhaust that is rich in gaseous C is an ideal environment for graphene synthesis because it provides adequate C for thin sheet synthesis along the substrate.

To synthesize graphene, a substrate was placed into the exhaust channel of the combustor with the tip of the substrate at the edge of the combustor flame. Due to the C solubility of Cu and size of the combustor channel, a Cu wire (rather than a mesh, which is seen in many other synthesis methods) was used as a substrate [21]. Results have shown that FLG and other types of

C can be synthesized upon the Cu wire with 20 s of deposition time and minimal sample preparation (simple degreasing procedure). The simplicity of the synthesis apparatus and speed of synthesis make microcombustion an exciting and promising form of FLG synthesis. Synthesis time is two orders of magnitude more rapid than current methods and the method does not require highly specialized tools or chambers for success.

1.4 Raman Spectroscopy

Detection of graphene relies primarily on spectroscopic methods to confirm the chemical bond states allowing identification of the signature C-C bonds, specifically raman spectroscopy. The instrument used for the project was a Renishaw-Smiths Detection Combined Raman - IR Microprobe. The instrument is pictured below in Figure 3.

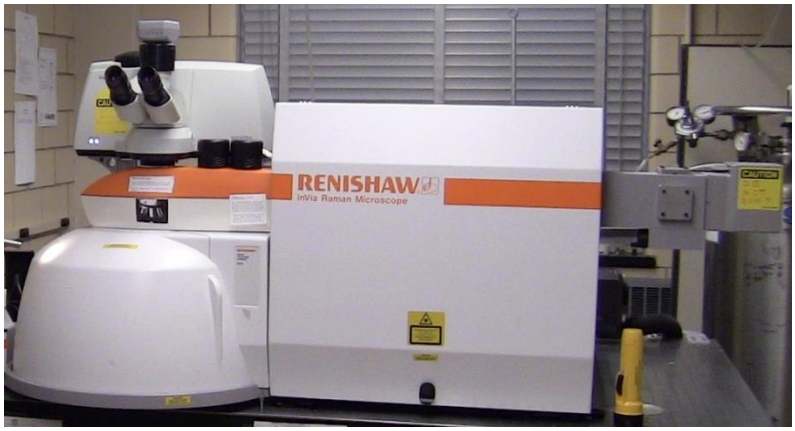


Figure 3: Renishaw-Smiths Detection Combined Raman-IR Microprobe. The microprobe's raman spectroscopy features were utilized throughout the project to characterize samples' chemical components and structure. The instrument was provided by the Analytical Spectroscopy Laboratory in Evans Laboratory at The Ohio State University. All instrument training and assistance was provided by Dr. Gordon Renkes.

Raman spectroscopy consists of subjecting a sample to laser light at a known frequency and implementing band filtering techniques to selectively measure the intensities across range of frequencies of light to determine the frequency of photons that are emitted back from the sample.

The laser light used in the project was 514 nm, a green wavelength of light. When looking for graphene and other carbon forms, there are three characteristic peaks seen through Raman spectroscopy. These peaks are known as the D peak (1350 cm^{-1}), G peak (1580 cm^{-1}), and 2D peak (2700 cm^{-1}). Figure 4 displays a response characteristic of graphene with each peak labeled.

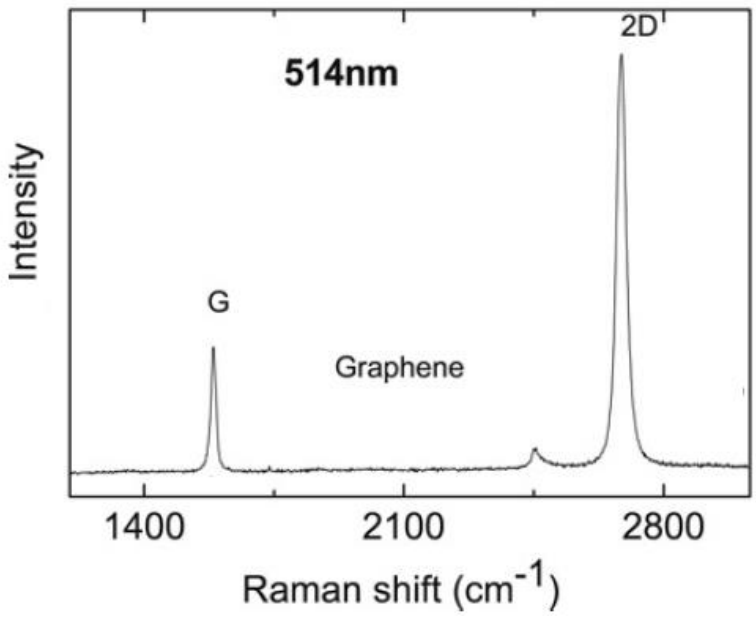


Figure 4: Raman spectrum of pristine graphene from Ferrari et al. [22]. Lack of D peak (1350 cm^{-1}) indicates that there is no disorder in the sample. G peak (1580 cm^{-1}) indicates the C=C bond and 2D peak (2700 cm^{-1}) is the second order resonance of the D peak. It can be seen that there is a roughly 1/3 ratio between the intensities of the G to 2D peaks.

Each peak is indicative of a characteristic of the carbon sample. The D peak is the first resonance mode of the hexagonal structure of graphene. Under Raman spectroscopy it is only visible if the sample is disordered. In highly ordered graphene it is not present due to the highly ordered nature of the sample, for this reason it is not seen in Figure 4. In many other forms of C, the D peak is seen due to the disordered structure of the C atoms. Therefore, the presence of the D peak is used as an indicator of soot, graphite, and other carbon forms within the sample. Due to the nature of the response of this peak, the D peak is used a measure of sample disorder with increasing intensity indicating increasing disorder. The G peak indicates a carbon to carbon bond

(C=C) with sp^2 hybridized bonding. This response is therefore very strong for all forms of C including, but not limited to, soot, bulk graphite, graphene, few layer graphene (FLG), highly ordered pyrolized graphite (HOPG), and single and multi-walled carbon nanotubes. Finally, the 2D peak is the second resonance of the hexagonal structure, hence the name 2D [22, 23]. The 2D peak is seen in the absence of the D peak due to the highly ordered nature of the sample structure. The molecular structure of highly ordered graphene emits photons at the D wavelength only when excited by infrared light; the second resonance is visible at wavelengths of light used in raman spectroscopy. For this reason, when graphene is present, only the G and the 2D peak are seen. Additionally, the ratio of the G and the 2D peak can be used to determine the number of layers seen within the C sample, with a .35 D-2D ratio being indicative of single layer graphene [22, 23]. This ratio can be used to determine whether the sample is graphene, few layer graphene, or bulk graphite.

In addition to the peak ratios, the overall raman spectrum response of each type of C can be used to determine which form of C is present upon a substrate. For this reason the spectrums for soot, bulk graphite, and HOPG have been presented in Figures 5, 6, and 7 respectively. Comparing the three figures allows a qualitative measure of the differences between the raman spectrum of the three types of C and that of FLG which is seen in Figure 4.

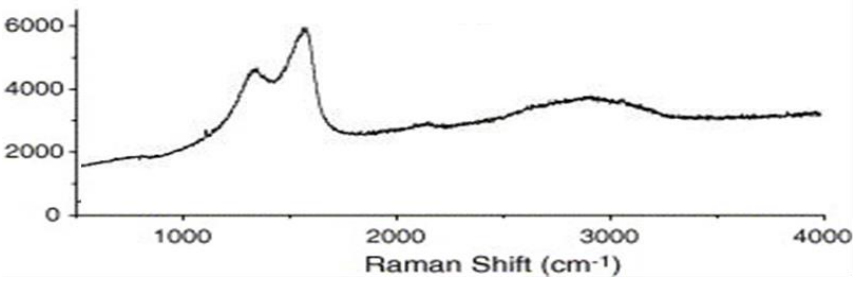


Figure 5: Raman spectrum of soot under 514 nm laser [24]. Very strong D and G responses are noticeable with a shouldered nature of the D and G peak. A less clear broad response is seen in the 3000 cm^{-1} region.

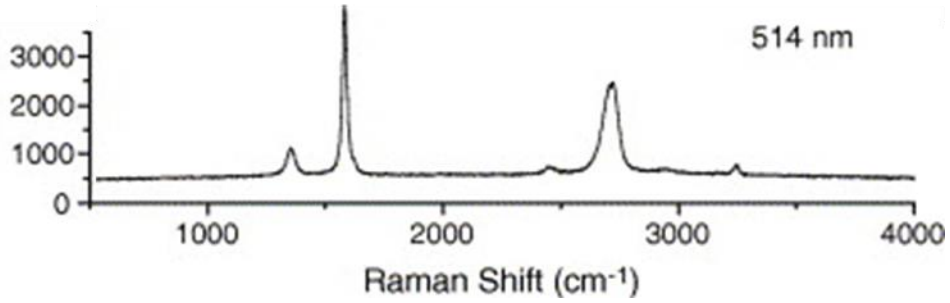


Figure 6: Raman spetrum of bulk graphite under 514 nm laser [24]. Very strong G peak as well as a strong 2D response. Due to mild sample disorder, a D peak is also visible, but the intensity of the D peak is much reduced due to the generally ordered nature of the graphite.

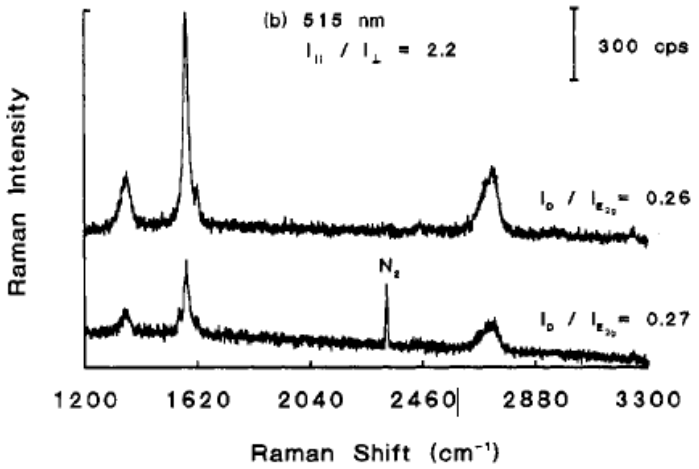


Figure 7: Raman spectrum of highly ordered pyrolitic graphite (HOPG) under 515 nm laser [25]. The response seen is very similar to that of bulk graphite, but the peak ratios between the D and G peaks have also been indicated (.26 and .27). These ratios can be used to detect HOPG as well as the relative sizes of the D, G, and 2D peaks that are seen in the image.

During sample analysis, visual microscopy allowed the spectrometer to be aimed and facilitated detection of areas of the sample that were of interest. The procedure was usually done at a 50 x magnification as the graphitic regions were on the order of a few microns in length and width. Once a region had been found, the laser light was focused and a reading was taken using a band filtering technique. Once the results across a range of wavelengths were recorded, normalization and base-lining functions were run on the data. The most important of the three techniques was base-lining, which helped to remove substrate interference known as

luminescence from the data. A before and after example of Raman data can be seen in Figure 8. The technique allowed the user to pinpoint only the peaks that were being seen from C and other substrate contaminants. A detailed description of instrument use is attached with other process sheets in Appendix 1.

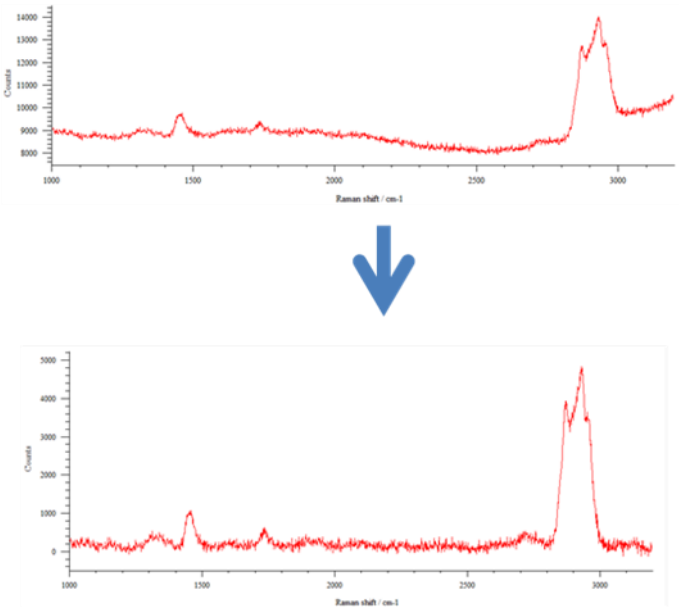


Figure 8: Sample of raw raman data (pictured top) and curve fit and baselined data (pictured below). The axes have not been expanded as the data is not meant to show specific counts and wavelengths, but rather overall curve changes in the data to provide a qualitative understanding of the data analysis technique.

2. METHODS AND MATERIALS

2.1 Overview

An alumina microcombustor unit fueled by methane and oxygen gas was used for all graphene deposition throughout the project. Fuel flow rate was regulated using a 247D Four Channel Power Supply/Readout (MKS Instruments) and corresponding 1179A Mass-Flo controllers (MKS Instruments). The microcombustor unit consisted of channels machined by computer numerical control (CNC) into an alumina block. The alumina base was covered with a quartz top (for flame imaging) and connected to alumina inlet channels (for fuel delivery). The combustor and deposition process was developed and characterized during previous work in the

MSNS Lab. A step-by-step discussion of the deposition process is included in Appendix 1, Graphene Deposition Process Sheet. The combustor is pictured below in Figure 9.

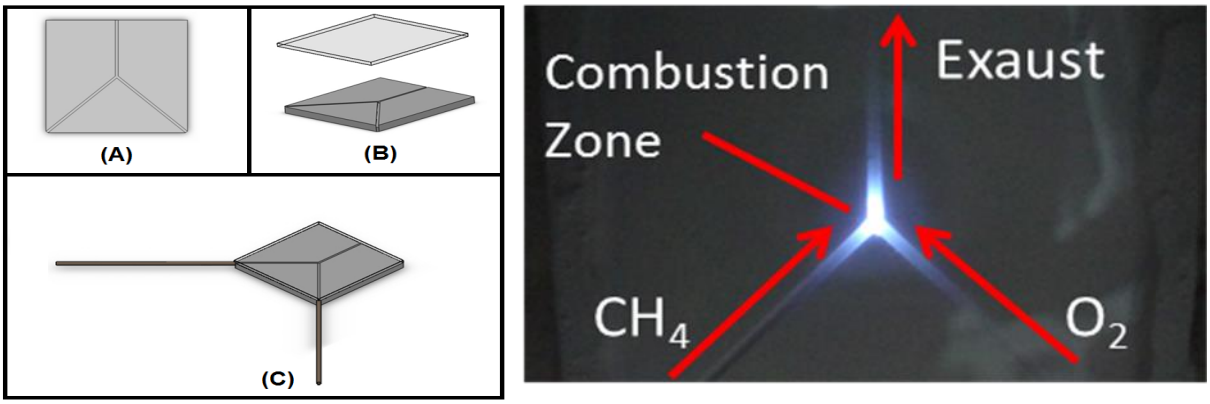


Figure 9: Prakash Group Alumina Microcombustor [23]. The microcombustor consists of an alumina base (A), a quartz top (shown unattached in B), and two fuel inlet tubes (shown attached along with quartz top in C). The microcombustor is shown during operation in the image on the right, with inlet gases, outlet flow, and combustion region indicated. The microcombustor unit consists of 5 cm alumina squares with channels that are 1.12 mm x 0.8 mm (LxD).

The project aimed to produce a transfer process through testing a variety of techniques, some methods were novel and others were similar to existing techniques that have been published. The project investigated the success of these techniques for removing FLG flakes from a round substrate; this differed from any methods seen in literature as the majority of existing techniques occur on a flat substrate. Additional challenges unique to the project stemmed from the small region along the wire in which FLG was located. A schematic can be seen below in Figure 10 that displays the various types of C found along the wire. FLG is seen in a 20 μm band that is located 40 μm from the tip of the wire [13]. Additional information about the deposition method and growth mechanism for C seen on the wire can be found in the Kellie paper published in RSC Advances [13]. The methods attempted varied from purely mechanical to purely chemical and finally a combination of both mechanical and chemical

elements. A discussion of each technique and the materials and methods pertaining to each is presented here.

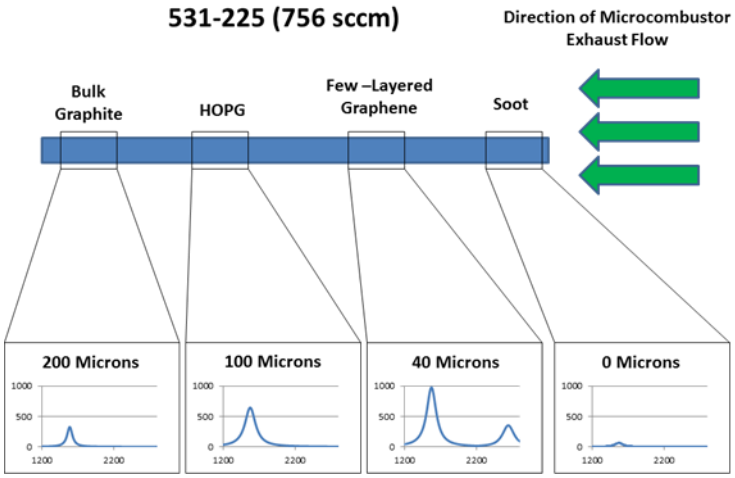


Figure 10: Schematic of the different types of C found along the Cu substrate [13]. Soot is seen at the tip, FLG at 40 μm, highly ordered pyrolitic graphite at 100 μm, and bulk graphite at 200 μm. The exhaust flows away from the tip as it is pictured in the figure. This specific configuration of C is seen most clearly at the 756 sccm total flow rate (531 sccm CH_4 – 225 sccm O_2 at standard atmospheric pressure). Also pictured are the raman spectroscopy responses for each type of C.

All liquid chemicals were measured using a 10 mL graduated cylinder (Tekk) and all temperatures indicated were recorded using an alcohol thermometer (McMaster-Carr). Any samples that required heating were placed upon an Isotemp hot plate (Fisher Scientific).

All "Si squares" in the discussion below consist of silicon wafers that have been cut with a diamond scribe to create approximately 1 cm x 1 cm square dies. The individual steps of the process can be seen in Appendix 1, Si Square Process Sheet.

A variety of methods were attempted with a wide spread of transfer mechanisms used for each method. Below in Figure 11, a flow chart is presented that gives a basic lay out and flow of different methods and the categorization of each technique. Each method will be discussed throughout the paper in detail.

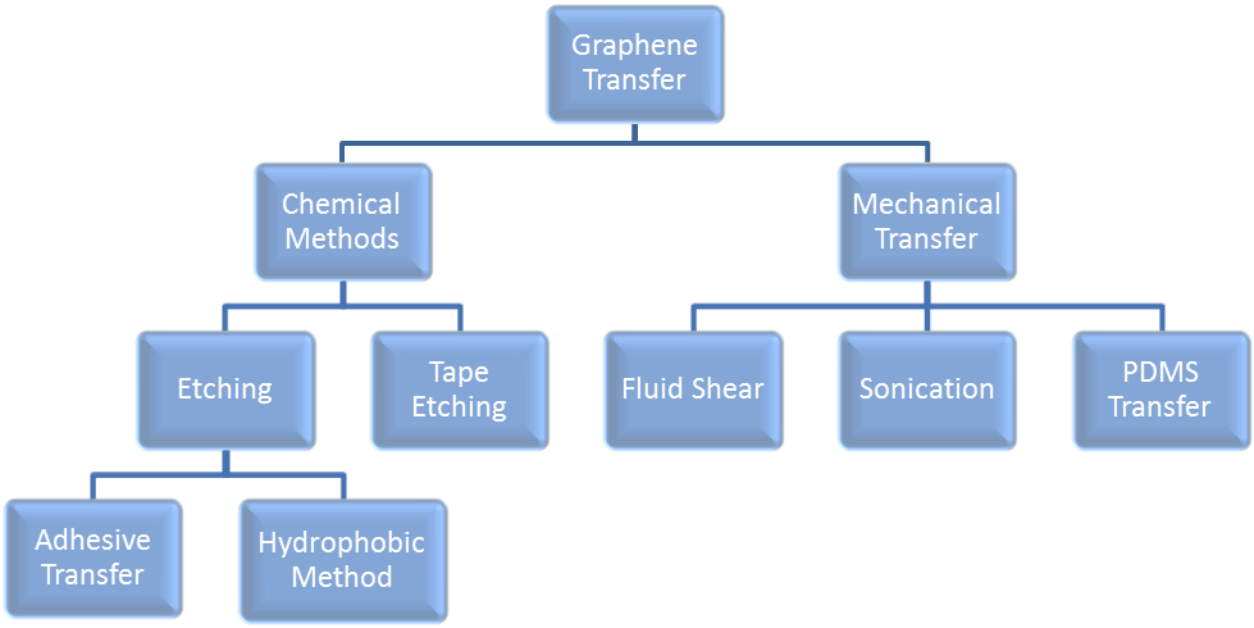


Figure 11: Transfer Process Flow Chart. The two main categories were chemical and mechanical transfer. Most processes could be easily categorized into one of these two subsections. Methods such as adhesive transfer and the hydrophobic method were a subsection of the etching process and sought to improve and expand upon the etching method.

Instructions for all following methods and processes can be viewed in Appendix 1.

2.2 Mechanical Transfer Method

The first method that was attempted was a simple shearing method that aimed to utilize normal as well as shear force along the substrate surface to peel the graphene from the substrate. The Cu wire first underwent the deposition process to synthesize FLG along the wire tip. The Cu wire tip was placed on a square of Si and force was applied to the top face of the substrate using an additional Si square. After force was applied, both rolling experiments as well as dragging experiments were conducted. Rolling was meant to transfer the FLG in a process similar to stamping, while the dragging experiments were conducted in an attempt to apply only

a shear force to the FLG. The latter of these methods was meant to tear the FLG from the substrate. A schematic of the process can be seen below in Figure 12.

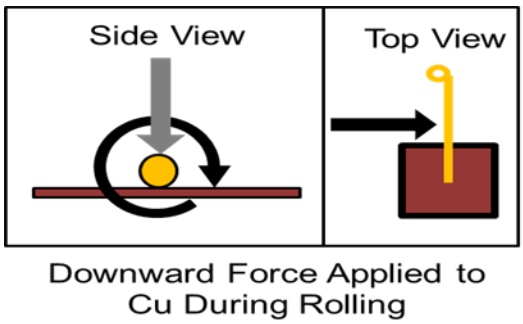


Figure 12: Mechanical transfer method. Force was applied to the Cu sample (pictured in yellow) normal to the Si substrate (shown in side view on left) and the Cu substrate was then rolled along the Si surface to attempt transfer of FLG to Si.

2.3 Chemical Etching

The chemical etching method was performed with the goal of removal of the underlying Cu substrate with acids to leave only C. The Cu substrates were placed on Si squares and then into acid in order to transfer C to Si once all Cu had been dissolved. The tests were completed with a variety of acids. The acids used in the tests were acetic acid, a commercial copper etchant, Transene CE-100 ($FeCl_3$), and a nitric acid (HNO_3)/H_2O solution. Each test consisted of placing the tip of a Cu wire with deposited FLG on a Si square. After setting the sample upon the Si, the Si square was submerged in acid in a standard 250 mL. A final setup schematic is presented in Figure 13. It was hypothesized that the adhesion force between the Si and the FLG would be enough to keep the FLG from floating away from the Si substrate during tests. The length of the etch process, visual results, and the effects on the sample was recorded for each of the tests.

Initially all acids (acetic, $FeCl_3$, and HNO_3) were tested at room temperature (~22°C). A second set of tests were attempted with CE-100 heated to 60°C (optimal reaction temperature

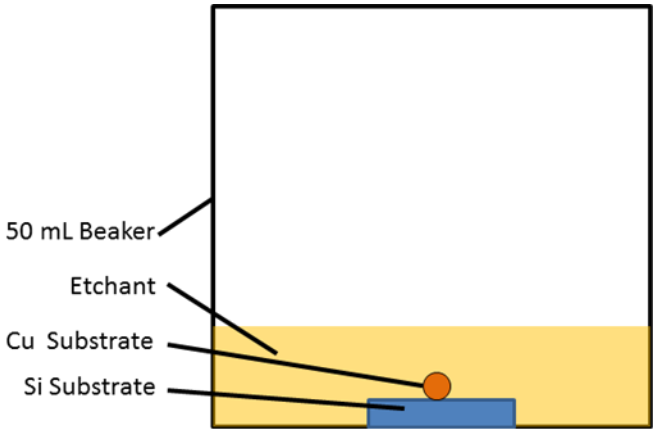


Figure 13: Chemical Etching Experimental Setup. Etchant is poured into a 250 mL beaker and Si substrate is placed into beaker with a Cu substrate placed on Si substrate. Cu substrate eventually dissolves during experiment.

indicated by manufacturer). A third set of tests were attempted utilizing a range of HNO_3 concentrations. After each test the Si squares were examined using visual microscopy as well as Raman spectroscopy to determine chemical components of the residue for each etch process and to search for FLG.

In an attempt to decrease the amount of remaining etching products such as Cu residue and un-etched Cu substrate particles, some Si wafers underwent a simple cleaning process. The process consisted of dipping the Si wafers that were covered in etchant products into a beaker of H_2O using a simple pair of tweezers to grasp the Si. After a single dip and 5 second dwell in the H_2O, the samples were allowed to dry before analysis.

2.4 Adhesive Transfer

The results of the chemical etching process indicated that FLG was no deposited on the Si during the etch process and was most likely lost within the beaker; further discussion of these results is presented in the results and discussion section. The adhesive process was developed with the goal of trapping FLG on the Si wafer to help increase retention of C during the etch process. Prior to undergoing the etching process, the Cu substrate was adhered to the Si square

using commercially available adhesive (Instant Krazy Glue All-Purpose). Initial tests were performed by using the applicator brush provided by the manufacturer to spread the adhesive across the Si. Results indicated that etch rates varied with the amount of Cu sample covered by adhesive. In order to increase etch rates and repeatability of the process a "screen-printing" method was developed. The "screen-printing" method consisted of applying adhesive to the Si square and using a razor blade to spread and skim the adhesive across the Si surface until a thin layer remained, a schematic is seen in Figure 14. Scribe marks were added to the surface of the Si square as well to indicate the region of the Si square that should be most carbon rich. This last step was added to increase ease of sample analysis and spectroscopy by denoting region where C should be located. A schematic of the adhesive application method has been presented below in Figure 14.

The combined Si wafer and Cu wire unit can be seen in Figure 14. After the substrate was adhered to the Si square, the combined unit underwent the chemical etching process. The adhesive method samples were only tested in $FeCl_3$ and the $HNO3/H_2O$ solution, this decision was made based on the results of the chemical etching process which indicated the two etchants were most effective at removing the Cu substrate. The resulting adhesive residue and Si wafers were then analyzed under Raman spectroscopy and visual microscopy to determine if there was any change from the results of the chemical etching method.

2.5 Single and Double Sided Tape Transfer

The tape transfer method was developed based upon the results of the mechanical transfer method. The method's aim was to increase the amount of force that could be applied to the FLG

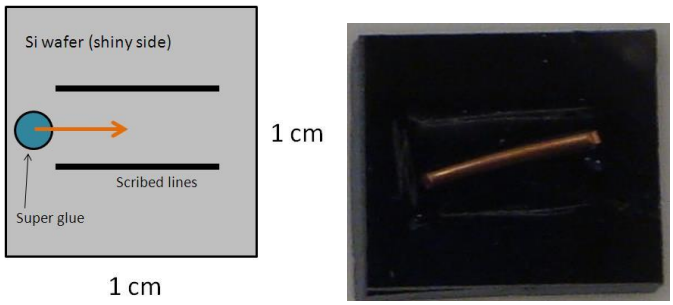


Figure 14: Adhesive method preparation. A thin layer of commercial adhesive was spread with a razor blade across the surface of the Si substrate (shown on left). Final experimental setup for adhesive method with Cu substrate fixed to a Si substrate by commercial adhesive (shown on right). Etch marks indicate the region that was expected to be graphene rich after etching.

flakes during a peeling process. For single sided tape tests, after FLG was deposited, the Cu substrate was rolled along the adhesive side of the tape. The tape was then placed onto a Si square with the adhesive side facing the Si. During double sided tape experiments, the tape was first placed on Si wafers, then the Cu samples were rolled along the tape. Double sided tape was employed in order to place the FLG on the outer side of the tape, rather than trapping it between the adhesive and the Si. A schematic of both experimental setups (single and double sided) is presented below in Figure 15. This step aided spectroscopy as well as the ensuing solvent "etch" process.

Figure 15: Single sided tape experimental setup is shown on the left, the purple square is the Si wafer, yellow represents the transferred C, and the grey square represents the tape. The double sided experimental setup is shown on the right. The colored blocks represent the same materials as the single sided tape schematic.

After adhering the tape and Si, the samples were placed into a variety of solvents to chemically etch the tape substrate and adhesive. Tests were attempted with acetone, dimethylformamide, chloroform, and methoxyethanol to ensure that a variety of polarities could

be tested. After solvent etching, each Si wafer was examined with Raman spectroscopy to search for FLG and to determine the chemical components of etch residues.

2.6 Fluid Shear Method

The fluid shear method was developed with the goal of using viscous forces of water along the length of the Cu wire to remove the FLG flakes. The method was attempted with the goal of a strictly mechanical transfer method that would eliminate issues caused by residues that were seen in the chemical methods. It was also hoped that the strength of the fluid shear would be greater than the shear seen from the direct mechanical transfer method which was discussed above. The method consisted of placing a Cu wire with deposited FLG into a syringe. The end of the wire without FLG was glued to the inner wall of the syringe to prevent the wire from moving within the syringe during each test. The syringe was then slowly filled with H_2O by retracting the plunger. The water was then forced out quickly through the syringe tip. The liquid flowed past the wire tip and the viscous forces of the fluid along the wire tip peeled C from the substrate. The fluid exiting the syringe was then filtered through standard filter paper (Whatman) and the fluid was caught in a 250 mL beaker. The filter paper from each test was examined under Raman spectroscopy to search for C and other deposits from the wire.

2.7 Sonication Method

The sonication method was developed with the goal of mechanically removing the flakes by using ultrasonic pulses (40 kHz). Cu wires with deposited FLG were placed into 250 ml beakers containing 50 mL of H_2O. The beakers were inserted into the corresponding sonicator slots for 60 minutes. The resulting fluid was filtered through standard filter paper (Whatman). The filter paper from each test was examined under Raman spectroscopy to search for C and other deposits from the wire.

2.8 Hydrophobic Method

The hydrophobic method was developed as a combination of etching and mechanical transfer. The method aimed to exploit the hydrophobic nature of graphene. Copper wire tips were placed on Si squares and then placed in HNO_3/H_2O solution inside of the top portion of a pipette. The experimental setup can be viewed in Figure 16.

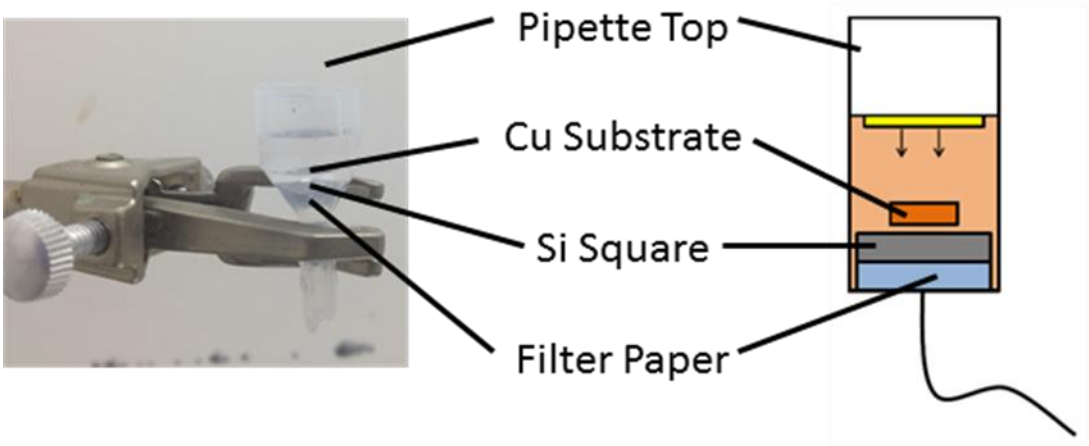


Figure 16: Hydrophobic Method Experimental Setup. Actual setup pictured on the left, consisting of a pipette tip filled with etchant and containing a Cu tip on Si square and filter paper at the bottom to catch etchant products. A diagram is pictured on the right, as imaging of actual set up is difficult and does not provide a concise picture of the setup. Floating graphene is represented on the right as the yellow square at the top of the etchant.

As the Cu substrate etched the FLG was released from the substrate. Due to the hydrophobicity of graphene the FLG flakes rose to the surface of the fluid. After the substrate etch reached completion the solution was removed slowly from the pipette using a syringe. After the fluid was removed, the Si samples were analyzed using Raman spectroscopy to check for sample contamination and deposited C across the surface of the Si.

2.9 PDMS Transfer

The PDMS transfer method was used with the goal of removing C deposits from the Si squares after completion of the hydrophobic method described above. Prior to the hydrophobic method, PDMS was cured in a circular plastic container and the solidified PDMS was then

removed from the container. After completing the hydrophobic method, the cured PDMS was pressed onto the surface of the Si square to remove C and other etch products. Visual imaging and detection of C deposits were possible due to the transparency of the PDMS. Raman spectroscopy was also conducted on the PDMS samples.

3. RESULTS AND DISCUSSION

3.1 Mechanical Transfer

The results of the mechanical transfer method indicated that no C or FLG were transferred. Raman spectroscopy and visual microscopy were not able to detect any form of C deposits upon the Si squares. It was expected that the adhesion forces between the Si substrate and the FLG (.151 J/m^2) [26] was greater than the adhesion forces between the FLG flakes and the Cu substrate (.72 J/m^2) [27] which would lead to transfer of the flakes from Cu to Si. The results for both the rolling technique and the sliding technique were identical. The similar results indicate that the bond force overcame the friction force in both cases. The results indicate that direct transfer is not possible from a Cu substrate to a Si substrate.

3.2 Chemical Etching

Cu substrate etching was attempted with acetic acid, CE-100 ($FeCl_3$; Transene, Inc.), and nitric acid (HNO_3). The etching results indicated that acetic acid was completely ineffective for substrate etching and no changes were seen in the Cu. Results for unheated CE-100 varied greatly with a shortest etch of ~ 6 hours and the longest etch lasting > 24 hours. Upon consulting the manufacturer, etch tests were attempted with CE-100 heated to 40°C. Etch times decreased significantly with the shortest etch ~ 1.5 hours and the longest etch at ~ 6 hours. Throughout the CE-100 tests etch time consistency was not achieved. This may have been a function of amount of solution stirring seen between each test. This hypothesis was not investigated in depth because solution stirring was not an ideal condition for substrate etching due to disturbance of C from the

Si substrate that it would cause. CE-100 was designed to etch thin films with large surface areas and was not as effective on wire substrates with smaller surface areas (on the scale <10 mm^3). Increasing energy into the reaction via heating did decrease overall etch times to less <6 hours, but it did not improve consistency of reaction times to a reasonable level (desired goal was to have etch tests that were of similar times on the range of a few minutes, a range of a few hours was achieved).

Due to the inconsistency of the CE-100 tests, HNO_3 was used due to the increased strength of the acid. A variety of ratios between H_2O and HNO_3 were attempted, ranging from 1:1 to 6:1. Etch times as low as 20 minutes were exhibited during the HNO_3 tests. Results did not appear to decrease in etch time beyond 2:1 H_2O-HNO_3 so all future etch tests were performed with this ratio. Greater consistency was seen with the H_2O-HNO_3 solution that CE-100 leading to all future substrate etching to be performed with the solution rather than CE-100.

Once a consistent etch rate had been determined, the Si squares were analyzed via Raman spectroscopy. The results indicate that the surface of the Si contained flakes of C, but was also contaminated with unetched Cu and etchant products. A characteristic Raman response is seen below in Figure 17 for C flakes seen on the surface of the Si squares. The D and G peaks can be seen clearly, indicating highly disordered C. This response is indicative of soot, but there are also minor peaks at higher wavelengths (2880 cm^{-1} and 2950 cm^{-1}) in the response. These peaks are attributed to etchant products and unetched Cu on the surface of the Si. The presence of C on the Si surface is an indication of successful transfer of C, but the additional products on the Si show that the carbon is contaminated with etchant residue and even if FLG were present, it would not suitable for application.

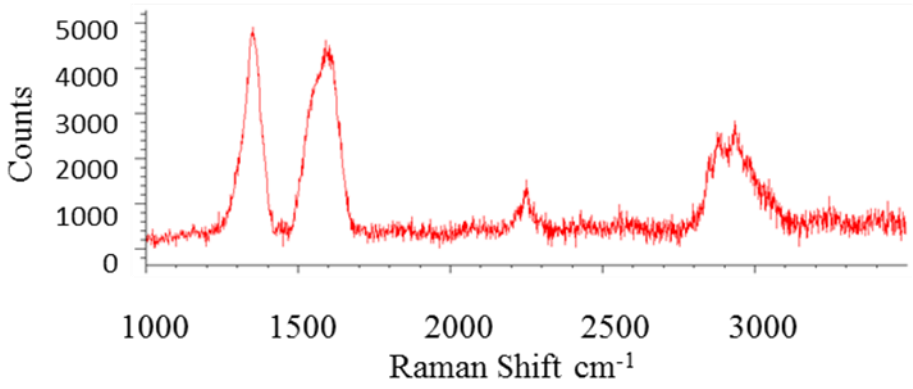


Figure 17: Raman Spectrum of Chemical Etching Samples. Carbon peaks can be seen at ~1350 cm^{-1} and ~1580 cm^{-1}. Additional peaks are seen at ~2250 cm^{-1}, 2880 cm^{-1}, and 2950 cm^{-1}.

3.3 Adhesive Transfer

Upon completion of Cu etching the remaining adhesive residue was analyzed via visual microscopy and Raman spectroscopy. An image of the Si square and remaining adhesive is shown below in Figure 18. It can be seen that all Cu substrate has been removed and only adhesive and any encased particles within the adhesive remain upon the surface of the Si.

Figure 18: Si Square with remaining adhesive residue (Pre-etch location of Cu substrate indicated)

Visual microscopy showed that regions of C had been trapped within the adhesive. Figure 19 below shows an image of adhesive that had been removed from the Si, the regions where C are present have been indicated.

To confirm the presence of C in the indicated regions, Raman data was collected for each location. A characteristic Raman spectrum is shown below in Figure 20.

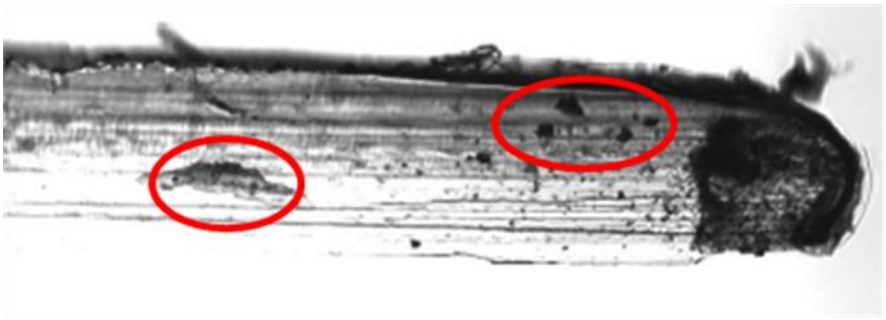


Figure 19: Adhesive with encased C regions shown, removed from Si substrate. C regions are indicated within red circles and appear as darkened areas within the lighter adhesive. The C regions consist of C that was deposited on the Cu surface during deposition and then was peeled from the substrate once the adhesive had set. Large dark region on the right is due to curvature of the end of the substrate and is a visual artifact of the sample, not indicative of C regions.

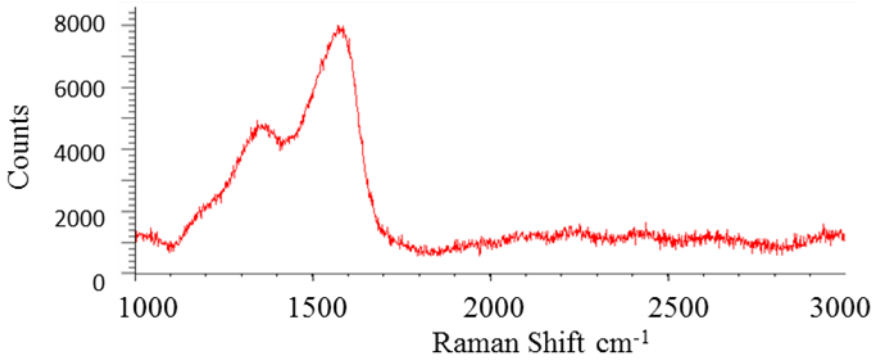


Figure 20: Raman Spectrum of Encased C. D and G peaks are seen, with other very minor peaks stemming from baselining techniques and curve fit that was applied to the data.

A strong D and G peak are present, similar to the results seen in the chemical etching method. It can be seen that the additional peaks that were seen in the chemical etching method are not present in the response. This indicates a much more pristine C, even though the C present is again only soot. These results show successful transfer of C and success in limiting the amount of etchant residue that is seen on the sample.

While successful transfer of C was exhibited, the results of the adhesive method posed an additional problem that was not seen in the chemical etching method. The transferred C was encased in adhesive which limited the ability to use FLG in applications. Attempts to dissolve the adhesive with acetone led to partial dissolution of the adhesive. The partial dissolution of the

adhesive left thick adhesive residues on top of the Si sample which did not allow for FLG raman spectrum to be detected. Rinsing of the adhesive led to total loss of C and other materials from the surface of the Si. These results indicated that, despite successful transfer from the Cu substrate, transfer to Si from the adhesive would not be possible.

3.4 Tape Transfer

A variety of solvents were tested on the tape to which the C had been transferred. Acetone, chloroform, dimethyloxyformamide, and methoxyethanol were the solvents that were used to attempt tape dissolution. Acetone yielded a thick residue during all tests. Acetone partially dissolved the adhesive as well as the substrate, but the entire sample was contaminated by a viscous glue based residue. Dimethyloxyformamide, and methoxyethanol yielded similar results in which the tape adhesive was fully etched, but the tape substrate was partially etched with a corresponding residue remaining upon the surface. The residue seen for these two solvents was less viscous and also less thick than the acetone residue, but the entire Si square was still contaminated with partially etched tape. Finally, chloroform produced no change in the tape samples. The above results were similar for both the single sided and the double sided tape. The residue seen across the face of the Si contaminated the C regardless of the orientation of C on the tape.

Figure 21 shows the Si squares after the acetone etching of the tape had been attempted. The residue can be seen on the squares on the left, a control Si square which has not undergone any processes is shown on the right for comparison.

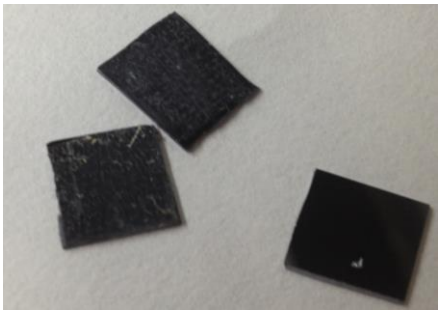


Figure 21: Si Squares for Tape Transfer Methods: Result Si squares are pictured with white tape residue covering the surfaces of both squares (Left) and control Si squares are pictured with reflective surface indicating a clean surface free of residue (Right)

Raman data was also collected on the surface of the Si squares after etching was completed. Figure 22 shows a characteristic response for regions that visually resembled C under visual microscopy. It can be seen that peaks indicative of carbon are present, but there are also major peaks at ~2907 cm^{-1} and ~2965 cm^{-1}. These peaks are consistent with the C-H bonds of methyl groups, CH_3. A main component of the adhesive on scotch tape is cyanoacrylates, which are rich in methyl groups. The presence of the methyl peaks as well as the C peaks confirm that all C regions that are present were covered in glue residue. The minor peaks present in the mid-range of the response were not able to be determined with 100% certainty due to the status of the tape recipe as a trade secret, but the minor peaks around 1460 cm^{-1} and 1750 cm^{-1} may represent CH_2 and H-N-H bonds respectively.

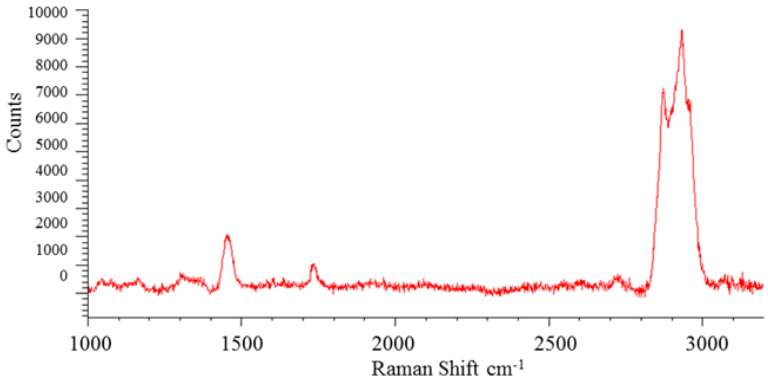


Figure 22: Raman Spectrum of Tape Transfer Samples. Peaks at ~2907 cm^{-1} and ~2965 cm^{-1} are indicative of methyl groups (CH_3) while the peaks at 1460 and 1750 are indicative of CH_2 and H-N-H bonds respectively.

3.5 Hydrophobic Method

During the hydrophobic method full dissolution of the Cu substrate was seen and small dark particles were seen to be floating on the surface of the etchant. Prior to draining the etchant these results showed some promise, but after draining the etchant results similar to those seen in the chemical etching method were exhibited upon the face of the Si squares. There was a noticeable decrease in the amount of C regions seen amongst the residue that remained on the Si squares. This is attributed to loss of C during the draining process and to sample disturbance from fluid movement that was not seen during the chemical etching method. It is hypothesized that much of the C was lost to the filter paper or to the syringe through which the etchant was drained.

3.6 Sonication

After sonication was completed, the Cu substrate was analyzed as well as the filter paper through which the sonication fluid had been filtered. Raman responses of the Cu indicated that all C had been removed from the Cu substrate. Raman data was collected only to 3000 μm, this is well past the region in which FLG is expected to be seen as was noted in the introduction. A characteristic response of the Cu substrate is seen below in Figure 23.

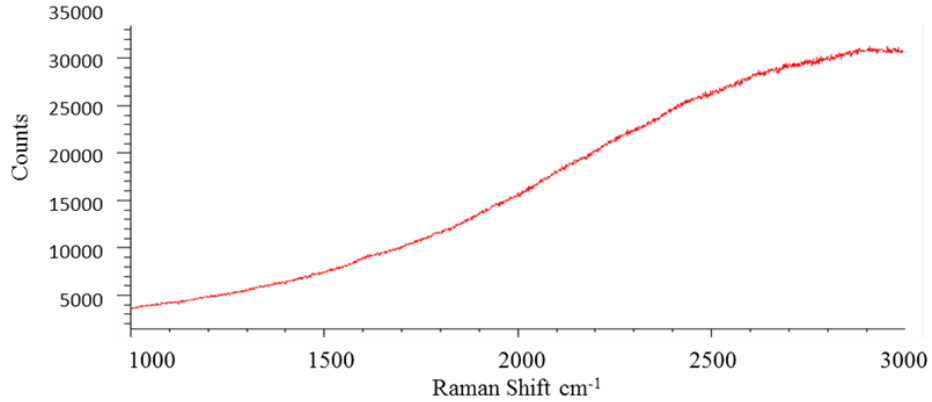


Figure 23: Raman Response of Cu Substrate After Sonication. No peaks are seen, which indicates a bare Cu substrate that has been cleaned of all C via sonication.

The smooth curve and increasing intensity of the response is luminescence from the Cu substrate. This type of response is typical of metal substrates, the lack of major irregularities or peaks indicate a bare substrate.

Visual microscopy and Raman spectroscopy of the filter paper through which the sonication fluid was filtered did not yield any evidence of C particles. It is hypothesized that all flakes were lost through the gaps in the filter paper, lost somewhere on the surface of the filter paper, or adhered to the surface of the beaker.

The lack of a C region on the wires or on the surface of the filter paper indicates that C and FLG was successfully removed from the Cu substrate, but capturing the C after removal from the surface was not achieved.

3.7 Fluid Shear

Visual microscopy of the Cu substrate after completion of the fluid shear method qualitatively indicated that a portion of the C had been removed from the substrate. Detection of C along the surface of the wire was more difficult than on Cu that had only undergone deposition. Raman spectroscopy indicated that the C regions present were similar to those seen on substrates that had undergone deposition. These results indicate that a portion of the C had been removed, but total removal of C (like that seen in the sonication method) was not achieved.

Visual microscopy and Raman spectroscopy along the surface of the filter paper yielded results similar to those in the sonication method. Upon completion of this second method it was determined that filter paper was not an appropriate method for capture of C from fluid.

3.8 PDMS Transfer

The results of the PDMS transfer method indicated that graphene had not been successfully transferred to the Si substrate. Characteristic raman data for the PDMS is presented below in

Figure 24. The results indicate two peaks at 2905 cm^{-1} and 2964 cm^{-1}. Such results are indicative of the methyl groups which have been discussed. PDMS is rich in such groups and this data indicates that the only material seen is PDMS. From these results it was determined that successful transfer of FLG was not seen from Si to PDMS.

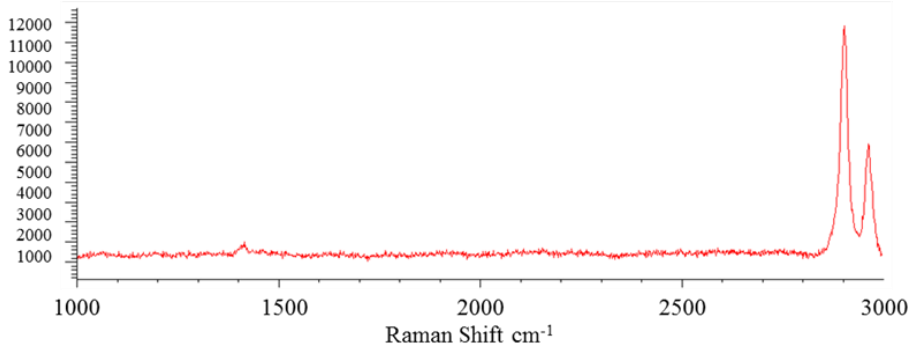


Figure 24: Raman Spectrum of PDMS Method. Peaks at 2905 cm^{-1} and 2964 cm^{-1} are indicative of cyanoacrylate residues.

4. CONCLUSIONS & FUTURE WORK

4.1 Conclusions

The overall conclusions of the project are that a variety of methods displayed successful transfer of C from the Cu substrate, but pristine transfer to Si was not exhibited. The methods that exhibited the most promise for pristine transfer were the fluid shear and sonication methods due to the physical nature of the transfer rather than a chemical transfer. Additionally, the hydrophobic method showed promise for removing graphene from the substrate and separating the C from the etchant and its products, but due to the etchant removal technique, successful transfer was not exhibited. The inability to successfully capture the flakes once they had been removed from the substrate severely hindered the success of all of these methods.

While many of the chemical methods produced interesting and informative results, none of the etching processes produced a method of transfer that did not contaminate the FLG. The adhesive and tape methods showed no promise for the ability to transfer graphene without

residue. The chemical etching process indicated an avenue for successful removal of the substrate, but the experiments showed a thorough lack of ability to separate the C from the Cu and etchant products.

4.2 Future Work

Future efforts on the project should be focused on developing new processes and further investigating the work that has been begun here. A wealth of data and knowledge has been produced that indicate avenues to successful transfer. Specifically, the methods that rely on physical methods of transfer should be further investigated. Separation techniques for C from fluid should be attempted. Devices such as a centrifuge or other methods of filtering the fluids should be investigated.

Upon successful transfer, the FLG should be implemented into a successful device as indicated in the project purpose. Graphene shows promise for a wide variety of applications as noted in the introduction which gives the project endless directions for continuation should FLG be successfully isolated. Graphene membranes, electronics, or reinforced polymers are all areas that show exciting new developments that are currently being investigated by many groups. Any or all of these areas could be investigated if this new method of graphene production is perfected.

REFERENCES

1. Kellie, B.M., *Carbon Nanomaterials Deposition in an Alumina Microcombustor*, Ohio State University, 2012, osu1338319539.

2. Borysiak, M., *Graphene Synthesis by CVD on Copper Substrates.* 2009.

3. Jianting Ye, M.F.C., Koshino, M., Russo, S., Inoue, S., Yuan, H., Shimotani, H., Morpurgo, A.F., Iwasa, Y. *Accessing the transport properties of graphene and its multilayers at high carrier density.* PNAS, 2011. **108**(32): p. 5.

4. Novoselov, K.S., *Electric Field Effect in Atomically Thin Carbon Films.* Science, 2004. **306**(5696): p. 666-669.

5. Lee, Y. *Synthesizing a Single Layer of Hetero-Epitaxial Graphene and Raman Spectrum at Different Layers of Graphene*. 2007. http://mxp.physics.umn.edu/s07/projects/s07_graphene/Default.asp

6. Beer, F.P., E.R.J.J., DeWolf, J.T. *Mechanics of Materials*. 4th ed. 2006, New York, NY: McGraw-Hill.

7. Debelak, B. and Lafdi, K. *Use of exfoliated graphite filler to enhance polymer physical properties.* Carbon, 2007. **45**(9): p. 1727-1734.

8. Cohen-Tanugi. D and Grossman, J, *Water Desalination Across Nanoporous Graphene.* Nano Letters, 2012. **12**: p. 3602-3608.

9. O'Brien, M., B.N., *CVD Synthesis and Characterization of Graphene Thin Films.* Army Research Laboratory, 2010. **ARL-TR-5047**: p. 24.

10. Seung Jin Chae, F.G., Kang Kim, K., Sung Kim, E., Hee Han, G., Min Kim, S., Hyeon-Jin S., Seon-Mi Y., Jae-Young C., Min Ho P., Woong Yang, C. Pribat, D., Hee Lee, Y. *Synthesis of Large-Area Graphene Layers on Poly-Nickel Substrate by Chemical Vapor Deposition: Wrinkle Formation.* Advanced Materials, 2009. **21**: p. 6.

11. Borysiak, M., *Graphene Synthesis by CVD on Copper Substrates.* 2009.

12. Reina, A., et al., *Large Area, Few-Layer Graphene Films on Arbitrary Substrates by Chemical Vapor Deposition.* Nano Letters, 2009. **9**(1): p. 30-35.

13. Sarkozy F, Robert; 1985 Dec. 3. *Method for Providing Sunstantially Waste-Free Chemical Vapor Deposition of Thin-Film on Semicondcutor Substrates*. United States patent US 4,556,584.

14. Kellie, B.M., Silleck, A., Bellman, K., Snodgrass, R., and Prakash, S. *Deposition of Few-Layered Graphene in a Microcombustor on Copper and Nickel Substrates.* RSC Advances, 2013, **3**: p. 7100.

15. Prakash, S., Glumac, N.G., Shankar, N., Shannon, M.A., *OH Concentration Profiles over Alumina, Quartz, and Platinum Surfaces using Laser Induced Fluorescence Spectroscopy in Low-Pressure Hydrogen/Oxygen Flames.* Combustion Science and Technology, 2005, 177(4), p. 793-817.

16. Prakash, S., Armijo, A.D., Masel, R.I., Shannon, M.A., *Flame Dynamics in Sub-Millimetre Combustors.* International Journal of Alternative Propulsion, 2007, 1(2/3), p. 325-338.

17. S. Prakash, R. Akberov, D. Agonafer, A. D. Armijo and M.A. Shannon, *Influence of Boundary Conditions on Sub-Millimeter Scale Combustion,* Energy Fuels, 2009, 23 (7), p. 3549–3557.

18. Miesse, C., et al., *Experimental observations of methane–oxygen diffusion flame structure in a sub-millimetre microburner.* Combustion Theory and Modelling, 2005. **9**(1): p. 77-92.

19. Miesse, C.M.M., Richard I.; Short, M., Shannon, M.A., *Diffusion flame instabilities in a 0.75mm non-premixed microburner.* 2005.

20. Miesse, C. M., Masel, R.I., Jensen, C. D., Shannon, M. A. and Short, M. *Submillimeter-scale combustion,* AIChE J., 2004, 50(12), 3206–3214.

21. Mattevi, C., H. Kim, and M. Chhowalla. *A Review of Chemical Vapour Deposition of Graphene on Copper.* Journal of Materials Chemistry, 2010. **21:** p 3324-3334.

22. Ferrari, A.C., *Raman spectroscopy of graphene and graphite: Disorder, electron–phonon coupling, doping and nonadiabatic effects.* Solid State Communications, 2007. **143**(1-2): p. 47-57.

23. Memon, N., Jafar Al-Sharab, S.T., Yamaguchi, H., Gonclaves, A.M., Kear, B., Jaluria, Y., Andrei, E., and Chhowalla, M. *Flame Synthesis of Graphene Films in Open Environments.* Carbon, 2011. **49**: p. 7.

24. A. Sadezky , H. Muckenhuber , H. Grothe , R. Niessner , U. Paschl, *Raman microspectroscopy of soot and related carbonaceous materials: Spectral analysis and structural information.* Carbon, 2005. **43**(8): p. 1731 – 1742.

25. Y. Wang, D.C. Alsmeyer, and R.L. McCreery, *Raman Spectroscopy of Carbon Materials: Structural Basis of Observed Spectra.* Chemical Materials, 1990. 2: p. 557-563.

26. Huang, R. *Grapehene Show of Adhesive Strength*. Nature Nanotechnology, 2011. **6**: p. 537-538.

27. Yoon, T., Cheol Shin, W., Yong Kim, T., Hun Mun, J., Taek-Soo, K., and Jin Cho, B. *Direct Measurement of Adhesion Energy of Monolayer Graphene As-Grown on Copper and Its Application to Renewable Transfer Process*. Nano Letters, 2012, **12 (3)**: p. 1448–1452.

Appendix 1

PROCESS SHEETS

Sample Preparation

1. Cut 3-4 cm of copper wire from spool using wire cutters.
2. Twist one end of wire around a spare combustor leg to create a coil to hold during combustion.
3. Straighten remaining wire for insertion to combustor channel.
4. Rinse sample with acetone twice. Dry sample with a Kim wipe after each rinse.
5. Rinse sample with isopropyl alcohol. Dry sample with a Kim wipe after rinsing.
6. Place sample in plastic Petri dish.

Sample Combustion

1. Open valves on Methane and Oxygen tanks.
2. Confirm that pressure to combustor is set to 100 psi.
3. Turn on flow controller using the on/off toggle on the left side of the control panel.
4. Allow the flow controller to warm up for 30 minutes before use.
5. Check flow levels using the set point toggles on each channel.
6. Set flow rates using set point screws on each channel (531 sccm methane, 225 sccm oxygen)
7. Turn on each channel
8. Ignite combustor a few inches from channel entrance using a lighter.
9. Reduce methane flow rate until flame enters channel, extinguish any flames at channel entrance.
10. Increase methane flow rate to desired set point.
11. Allow combustor to run for 15 minutes to ensure steady state has been reached.
12. Pick up prepared sample using pliers.
13. Insert sample into channel up to just before blue tip of flame. Leave sample in channel for 20 seconds. Rotate sample if desired.
14. Remove sample from channel once deposition time is reached.
15. Place sample in Petri dish for later analysis.
16. After all samples are completed, turn off channels (be sure to shut off methane channel first).
17. Close valves on both tanks.
18. Turn channels on and allow flow controller to run until flow rates decrease to zero.
19. Confirm that both tanks have been depressurized by checking that both regulator gauges read zero.
20. Turn off both channels and then the entire flow controller.

Si Square Creation

1. Remove an Si wafer from container and place on clean Kim Wipe.

2. Using a diamond scribe and a 6” scale, mark 1 cm by 1 cm squares.
3. When the desired number of squares have been laid out, use diamond scribe to further engrave squares to increase ease of breaking Si.
4. Using the edge of the lab table, apply force to Si square to create separation along scribed lines.
5. Continue this process along each line until all squares have been removed from Si wafer.
6. In the event of partial separation or separation that does not follow scribed lines, use wire cutters to trim the edges of the Si square to achieve required dimensions.
7. After cutting, place all Si squares in a clean 5 cm disposable Petri dish for storage.

Mounting Sample to Si

1. Depending on requirements of the experiment, either perform only cleaning process or clean and also deposit FLG on the Cu wire.
2. Cut Cu wire tip to .5 cm and place on clean Kim Wipe.
3. Remove Si square from storage dish and place on Kim Wipe.
4. Using a diamond scribe, engrave lines on the Si square to indicate where Cu substrate will be adhered.
5. Place a single drop of Krazy Glue on the Si square.
6. Using a razor blade spread the adhesive until a very thin layer is achieved.
7. Using tweezers, place Cu substrate on Si square within etched lines.
8. Allow 12 hours for adhesive to dry completely before performing tests on sample.

Copper Etching

1. Depending on the etchant desired, either mix 20 mL of desired HNO_3 solution or pour 20 mL of Transene CE-100 etchant ($FeCl_3$) into a 250 mL beaker.
2. If heating is required ($FeCl_3$) place etchant on hot plate and allow solution to reach desired temperature, monitor solution using standard alcohol thermometer.
3. Once solution has been prepared, use tweezers to place sample (either wire or Si with attached Cu) into etchant for experiment.
    a. If sample is Si with attached Cu, place Cu facing up and Si square backing on the floor of the beaker.
4. Monitor solution and samples until entire Cu substrate is dissolved.
5. Upon etch completion, use tweezers to remove Si square with as little disturbance to the Si and C as possible.
6. Dispose of all etchants properly. For HNO_3 dispose in acid container, for CE-100 dispose of in the CE-100 waste container

Mechanical Transfer Method

1. Perform FLG deposition process on Cu wire.
2. Place clean Si square on a clean Kim Wipe.

3. Place tip of Cu wire on Si square.
4. Using another clean Si square, place pressure on Cu substrate.
5. Simultaneously roll the substrate across the surface of the Si square on the table.
6. Store lower Si square in a clean disposable Petri dish for later analysis.

Adhesive Transfer

1. Perform Si square with attached Cu process.
2. Place sample in desired etchant (prepare solution using Chemical Etching Process Sheet instructions) to dissolve Cu substrate.
3. Using tweezers, remove Si square from solution with attached adhesive once all Cu has dissolved.
    a. In the event of adhesive layer separation, remove adhesive as well.
4. Store samples in clean disposable Petri dish for later analysis.

Single and Double Sided Tape Transfer

1. Perform FLG deposition process.
2. Cut a 1 cm piece of scotch tape (either single or double sided tape depending on the experiment.
3. Roll .5 cm of the Cu substrate (measured from the tip of the wire) along adhesive of tape
    a. If single side tape is used, set adhesive free side on a clean Kim wipe while rolling. After rolling place adhesive side face down on a Si square.
    b. If double sided tape is used, place one side of tape on top of Si square. Once tape has been adhered to Si, perform rolling of Cu.
4. Place Cu substrate in clean disposable Petri dish for later analysis.
5. Place Si with attached tape into 20 mL of desired solvent.
6. Monitor tape while submerged in solvent, when no change has taken place for 30 min, remove substrate and place in clean disposable Petri dish for later analysis. Do not cover Petri dish until all visible solvent has evaporated.

Fluid Shear Method

1. Perform FLG deposition process.
2. Remove stopper from a standard 10 cc syringe.
3. Bend Cu wire so tip of wire points along length of syringe tip and base of Cu wire lays flat along syringe walls.
4. Use Krazy Glue to adhere Cu wire to walls of syringe.
5. Allow Krazy Glue to dry.

6. While adhesive is drying, place filter paper over a 250 mL beaker and secure with a rubber band.
7. Once glue is dry, fill syringe with DI water from back and replace stopper.
8. Force H_2O through syringe and filter exiting contents through filter paper and into beaker.
9. Allow filter paper to dry.
10. Placed dried filter paper into clean disposable Petri dish for later analysis.

Sonication Method

1. Perform FLG deposition process.
2. Fill 250 mL beaker with 50 mL of water.
3. Cut .5 cm of substrate (measure from tip) using wire cutters and place into a 250 mL beaker.
4. Place beaker in sonicator beaker holder.
5. Turn on Sonicator, and allow it to warm up for 10 minutes.
    a. Before operation, ensure sonicator contains water up to fill line.
6. Using the sonicator toggle, select timed sonication.
7. Set sonicator to run for 60 minutes.
8. Once sonication is complete, place filter paper over clean 250 mL beaker and secure with a rubber band.
9. Slowly pour contents of sonication beaker through filter paper.
10. Allow filter paper to dry.
11. Once filter paper is dry, place in a clean disposable Petri dish for later analysis.

Hydrophobic Method

1. Using a standard BIC lighter, burn and then twist a syringe about 1” from the base of the pipette bulb.
2. Cut off half of pipette bulb to create a container for which a fluid may be held.
3. Ensure that pipette tube has been melted and twisted shut by filling pipette top with water and searching for leaks.
4. Cut and place filter paper to fit across bottom of pipette bulb.
5. Place filter paper across the entrance to the tube of the pipette.
6. Place Si wafer on top of the filter paper, with shiny side facing up.
7. Place tip of Cu wire with deposited FLG onto Si wafer.
8. Using tape, attach pipette apparatus to side of 250 mL beaker.
9. Fill pipette bulb with desired etchant.
10. Allow all Cu to dissolve, similar to the chemical etching process sheet.
11. Once etch is complete, pierce pipette tube with a syringe and remove all etchant.

12. Remove Si wafer with tweezers and place in clean disposable Petri dish for later analysis.
13. Dispose of all etchant in proper waste containers.

PDMS Method

1. Mix 1:10 ratio of PDMS curing agent to PDMS pre-polymer in a plastic cup.
2. Stir for 10 minutes to ensure proper mixing of PDMS curing agent and pre-polymer.
3. Place plastic cup in vacuum chamber for 10 minutes, releasing and reapplying pressure every 2 minutes.
4. Repeat step 3 until all bubbles are removed from PDMS mixture.
5. Allow PDMS to set in bottom of cup.
6. Once PDMS has cured, remove PDMS from cup and place into clean disposable Petri dish.
7. Using a clean razor blade, cut PDMS into 1 cm x 1 cm squares.
8. Complete hydrophobic method to obtain Si wafer with etch products on surface.
9. Once Si with etch products is obtained, use 1 cm by 1 cm squares of PDMS to stamp on surface of Si square.
10. Apply pressure firmly with a finger and peel PDMS from surface.
11. Place PDMS square in a clean disposable Petri dish with surface that contacted Si facing upwards for later analysis.

Raman Spectrometer Operation

1. Turn key on laser power box to power up laser control unit.
2. Turn cooler unit to "run"
3. Press "On" on the laser power box to activate laser.
4. Monitor set temperature and running temperature on cooler unit until both numbers have converged and do not deviate from the set temperature (~25 minutes)
    a. During this process, monitor water flow out from cooler unit. If water is not flowing, turn off unit immediately and contact Gordon Renkes.
5. Once unit has reached set temperature, open WiREInterface on spectrometer computer desktop.
6. Press tools -> align -> autoalign. Allow autoalign to complete.
7. Press tools -> calibrate -> quick calibrate. Allow quick calibration to complete.
8. Press "new spectral analysis"
9. Run Si-514-pinhole to ensure proper calibration of instrument and laser.
    a. A single peak should be seen for Si at 1120 cm^{-1}
10. If 1120 cm^{-1} has been achieved, close spectral analysis. If not achieved, repeat steps 6-9.
    a. If proper calibration cannot be reached, contact Gordon Renkes
11. Press Measurement -> New Measurement
12. Press Measurement -> Setup Measurement
13. Select File Tab, Press Browse and select location of saved file.

14. Select Range tab and select 1000 minimum and 3000 maximum for bounds in order to capture data near 3 FLG peaks.
15. Close Setup Measurement box.
16. Place sample on Raman table
17. Select desired objective.
18. Focus on sample and determine area for analysis.
19. Repeat steps 17 and 18 if increased resolutions is required.
20. Once location for analysis has been determined, close door to spectrometer.
21. Using track pad, scan along surface of Cu for locations of interest.
22. When location for analysis has been located, press collect raman spectrum.
23. Repeat steps 21 and 22 until all desired data has been collected.
24. Once all data has been collected, remove sample from spectrometer table and close WIreInterface.
25. On laser controller, press "Off" and turn key on power unit once laser has been powered down.
26. Turn cooling unit to "Cool Down"
27. Download all data to jump drive.

Flow Meter Operation

1. Using toggle switch on left side of unit, turn on flow meter unit.
2. Allow meter to warm up for 30 minutes before use, during this time open valves on gas tanks to place flow meter valves under operational pressure.
3. Once unit has warmed up, using the flat head screw driver, toggle the set point for each channel and turn set screws until desired flow rate is achieved (for FLG synthesis, the unit should be set to 531 sccm CH_4 and 225 sccm O_2)
4. When it is desired to run the combustor, turn the toggle switches for the two channels into the "On" position.
5. Light combustor while fuel channels are on.
6. In order to extinguish the combustor, turn channels to "Off" position.
7. When microcombustor use is no longer needed, turn valves on fuel tanks to "Off" position and turn on combustor channels (this time DO NOT LIGHT combustor).
8. When flow channels read 0 sccm, turn channels to off position.
9. Use toggle switch on left side of unit to power down flow meter unit.

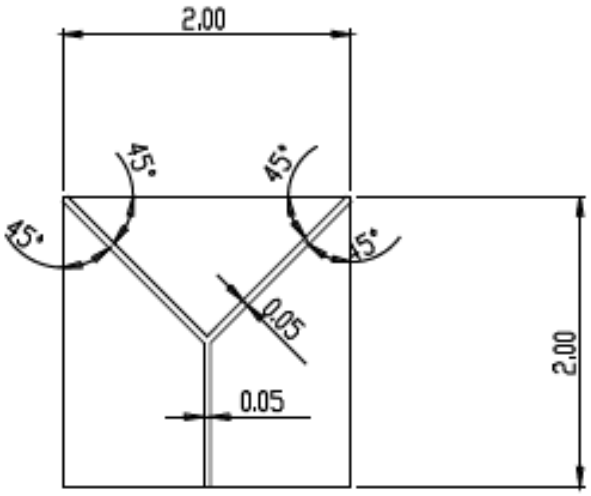
Flow Meter Channel Calibration

1. Determine equation constant for specific gas being used by consulting the equation constant table in the back of the MKS handbook for the flow controller.
2. Using the equation for atmospheric operation, plug in the specific gas constant from the table into the equation.
3. The equation and the constant will produce a value which relates to the proper setting for the flow aperture control dial.

4. On the back of the MKS Flow Controller, turn the control dial for the proper channel to the calculated value from the equation.
5. Repeat steps 1-4 for all gases and channels that are desired for use. When this is complete, flow meter is calibrated and ready for use.

Appendix 2

AutoCad Files for CNC Manufacturing of Microcombustor Unit



UNLESS OTHERWISE SPECIFIED: DIMENSIONS ARE IN INCHES SURFACE FINISH TOLERANCES: +/- .010 LINEAR ANGULAR	FINISH						DO NOT SCALE DRAWING	REVISION
	NAME	SIGNATURE	DATE				TITLE:	
DRAWN								
CHK'D								
APP'V'D								
MFG								
Q.A.				MATERIAL: MACHINABLE ALUMINUM			DWG NO. YDesign1	A4
				WEIGHT:			SCALE:1/1	SHEET 1 OF 1